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COLLECTION AND ANALYSIS OF DATA ON OXIDATIVE COUPLING OF METHANE

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MICROMEDIA

EXECUTIVE SUMMARY

The oxidative coupling of methane($2CH_4 + O_2 = C_2H_6 + H_2O$) is one of the promising processes for converting methane into higher hydrocarbons. A number of oxides, the metal oxides, the amphoteric oxides and the rare earth metal oxides have been tested for catalyst and many efficient catalysts have been developed. High yields of C_2 hydrocarbons(>20%) and very high selectivity to C_2(>90%) have been achieved. On the other hand, the reaction requires high temperatures(950-1200 K) and the hydrocarbon products are almost limited to C_2. The main reactions involved in the methane coupling are (1) the formation of ethane, (2) the non-selective oxidation of methane to CO_x in parallel to (1), and (3) the dehydrogenation of ethane to ethylene. The mechanism of the reaction is not simple, the methyl radicals are produced catalytically, and ethane are formed by the dimerization of the radicals in the gas phase. The rest of the reactions, the formation of CO_x and ethylene, take place catalytically and/or homogeneously depending on the reaction conditions employed.

The analysis of the published data surveyed in the present review indicates that the overall reaction of the methane coupling is mostly governed by the homogeneous reactions in the gas phase although the presence of a good catalyst is essential for an efficient initiation of the reaction. Many promising catalysts have been developped but the exact roles of the homogeneous reactions and the extent of their contributions to the final products are not clear yet. These should be clarified in the future researches for the development of this process. Particularly important is the study of the effect of the gas phase volume in the catalyst bed.

Another oxidative condensation of methane through the oxychlorination is also an interesting process particularly because it produces much higher hydrcarbonsn. However, the investigations have just been started and it is too early to assess the situation.

RESUME

Le doublement oxydant du méthane ($2CH_4 + \frac{1}{2}O_2 = C_2H_6 + H_2O$) est l'un des procédés prometteurs pour la conversion du méthane en hydrocarbures supérieurs. L'activité catalytique de certains oxydes, les oxydes métalliques, les oxydes amphotères, et les métaux des terres rares, a été testée, et nombre d'entre eux se sont révélés des catalyseurs hétérogènes efficaces. Les hydrocarbures en C2 ont été obtenus avec des rendements élevés (>20%) et une très grande sélectivité (>90%). Toutefois, cette réaction nécessite des températures élevées (950-1200K) et les hydrocarbures obtenus sont presqu'exclusivement limités à C2. Les réactions prédominantes impliquées dans le doublement oxydant du méthane sont (1) la formation d'éthane. (2) l'oxydation du méthane en CO_x en parallèle avec (1), et (3) la deshydrogénation de l'éthane en éthylène. Les mécanismes de ces réactions ne sont pas simples, les radicaux méthyl sont produits catalytiquement, puis ils se dimérisent en phase gazeuse en éthane. Les autres réactions, formation de CO_x et d'éthylène, sont catalytiques ou ont lieu en phase homogène, dépendant des conditions réactionnelles.

L'analyse des données publiées qui ont été considérées dans la présente mise-au-point montre que la réaction globale du doublement du méthane est sous la dépendance principale des réactions homogènes dans la phase gazeuse, bien que la présence d'un bon catalyseur soit essentielle pour une initiation efficace de la réaction. Plusieurs catalyseurs prometteurs ont été développés, mais il reste à élucider le rôle exact des réactions homogènes, et leur influence sur la nature des produits finaux. Ces aspects devront être clarifiés par des recherches futures pour permettre le développement de ce procédé. En particulier, il est très important d'étudier l'influence du volume de la phase gazeuse dans le lit catalytique.

La condensation oxydante du méthane par oxychlorination ou oxyhydrochlorination est un autre procédé intéressant, notamment parce qu'il produit des hydrocarbures bien plus condensés que ceux de la réaction de couplage oxydant. Toutefois les recherches n'en sont encore qu'au stade préliminaire et il est trop tôt pour l'évaluer.

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OXIDATIVE CONDENSATION OF METHANE

I. INTRODUCTION

Canada is abundant in natural gas and the utilization of natural gas is of great importance for the self-sufficiency of energy in future. Among various processes under investigation, the direct conversion of methane into higher hydrocarbons without going through syngas is particularly attractive and has drawn the wide interest of researchers. There are difficulties in the conversion mainly due to the high stability of the methane molecule and the thermodynamic disadvantage. For example, the dehydrogenation-polymerization of methane has a large positive change in free energy as

$$2CH_4 = C_2H_6 + H_2 \qquad \Delta G=71.0 \text{ kJ mol}^{-1} \text{ at 1000 K.}$$

Fortunately the thermodynamic disadvantage can be overcome by introducing an oxidant as

$$2CH_4 + O_2 = C_2H_6 + H_2O \qquad \Delta G=-121.6 \text{ kJ mol}^{-1} \text{ at 1000 K.}$$

The above oxidative condensation reaction is not limited to oxygen. For example, when chlorine is used as oxidant,

$$2CH_4 + Cl_2 = C_2H_6 + 2HCl \qquad \Delta G=-126.3 \text{ kJ mol}^{-1} \text{ at 700K.}$$

Theoretically the above oxidative reactions can proceed further in the reactor to produce higher hydrocarbons. When oxygen or nitrous oxide is used as oxidant, however, the products are almost limited to C_2 compounds,that is, the main reaction is the oxidative coupling of methane.

In this report, the published reports on the catalytic oxidative condensation of methane have been surveyed and analyzed. The results of oxidative coupling with oxygen and other oxidants supplying oxygen such as nitrous oxide

are reviewed in Chaps.II -IV and those of other oxidative condensation reactions are reported in Chap.V. Excluded from the present review are the papers dealing with the partial oxidation of methane which produce mainly oxygenated compounds. These reactions use the different types of catalysts and employ more moderate reaction conditions as reviewed by Pitchai and Klier[1]. Lee and Oyama[2] recently published an excellent review on the oxidative coupling of methane which is very useful in obtaining information on the reaction reported up to early 1987. The present report covers a total of about 110 papers and patents including most of those published in 1988. Surveyed but not cited in the report are papers presented at conferences without a full report in the preprint or proceedings. Finally in Chap.VI, we will make recommendations for future research which is essential for making these processes industrially feasible.

The following definitions and unit of terms will be used throughout this report. The term C_2 will represent both ethane and ethylene while C_{2+} includes all higher hydrocarbons as well as C_2. The total oxidation of methane to water and carbon dioxide always accompanys the oxidative coupling reaction. This undesirable side reaction will be called non-selective oxidation in this report and the products CO_2+CO will be generally represented by CO_x. The word conversion is used to indicate the conversion of methane unless otherwise stated, and is expressed as the fraction of methane reacted. Also the selectivity for C_2 products is designated simply as selectivity, and is defined as the ratio of the moles of methane converted to C_2 to the moles of total methane reacted. The yield is the product of the conversion and the selectiviy. The conversion, selectivity and yield are all expressed in percent. The contact time has been represented by a time constant, W/F, expressed in $g \cdot sec \cdot ml^{-1}$. The space time yield of C_2 will be abbreviated to STY and expressed in $\mu mol \cdot sec^{-1} \cdot g^{-1}$.

II. CATALYSTS

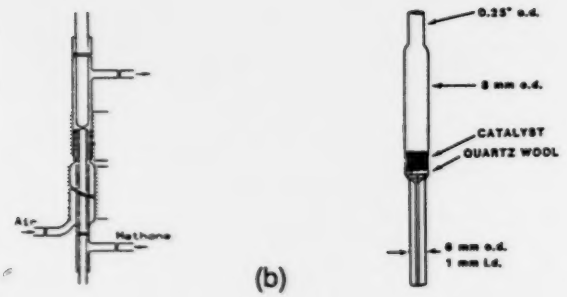
1. Mode of Reaction

(a) Cyclic feed In 1982, Keller and Bhasin reported the first systematic

screening of metal oxides for the oxidative coupling of methane[3]. They obtained most of the results by a cyclic feeding of reactants, that is, the catalysts were first oxidized by air followed by a short period of flushing with nitrogen and methane was then fed to the reactor. In the cyclic process in which the reactants are fed sequentially, only one gas is fed to the reactor at a time. Since there is no oxygen in the gas phase when methane is fed, the non-selective oxidation is limited resulting in generally good selectivity. It is also safe to operate. On the other hand, the catalysts must retain oxygen until methane is fed. For this reason the materials are generally limited to reducible oxides. Since the oxides are reduced during the reaction, they are not catalysts and the reaction is stoichiometric instead of catalytic. As a result, the coupling reaction is not steady:the conversion and selectivity change with time. Because of these features, few works have employed the cyclic mode of reaction[4-6] except for the mechanistic study of the reaction. Some oxides have been claimed in patents for the cyclic process of oxidative coupling[7-10].

(b) Cofeed Since Hinsen and Baerns[11] first reported high selectivities for the C_2 hydrocarbons by simultaneously feeding methane and oxygen over lead oxide catalysts, most investigations have used the cofeed mode of reaction. Usually a high ratio of methane to oxygen is employed to stay outside of the explosion limit. A diluent such as nitrogen and helium is often used with or without inert materials mixed with the catalyst to control the large heats of reaction from the coupling and non-selective oxidation reactions. Unless otherwise mentioned, results discussed in the present review were all obtained with a cofeed of reactants.

The reaction temperature is high for the oxidative coupling of methane, mostly in a range of 900-1200 K. Therefore, homogeneous reactions could also occur, and the volume of the gas phase in the reactor may play an important role in the reaction. Reactors of various designs were used to minimize the effect of empty space in the reactor as shown in Fig.1.



(a) (b)

Fig.1 Reactors. a[12], b[13]

2. Catalysts

A large number of oxides have been tried as catalysts for the oxidative coupling of methane. We have no intention of enumerating all reported catalysts in this section. It is also impossible to classify those materials unambiguously into several groups. Nevertheless, they are divided into three major groups here as a matter of convenience:(i) alkali and alkaline earth metal oxides;(ii) rare earth metal oxides;and (iii) other metal oxides.

Since Ito and Lunsford[14,15] first demonstrated that a lithium-doped magnesia was an active and selective catalyst for the oxidative coupling reaction, alkali metal-doped alkaline earth metal oxide catalysts have been studied by many workers. These catalysts are often called alkali-promoted magnesia and so on. However, the active centers of Li/MgO catalyst were found to be the surface Li^+-O^- species as discussed later. Therefore, it seems more appropriate to call it magnesia-supported lithium oxide catalyst. Nonetheless, the terms promoter and support are used conventionally in this review since the active centers are not always identified. This group includes alkaline earth metal oxides promoted by other alkali earth metals[16] and their halides[17] and also alkali metals/alkaline earth metal carbonates[18].

In 1981, Fang and Yeh[19] reported the formation of higher hydrocarbons by passing methane over a Th/SiO_2 catalyst at 1073 K with or without nitric oxide. This is probably the earliest paper reporting the oxidative coupling of methane. Otsuka et al.[20] made the first systematic comparison of catalytic performance for the methane coupling over the oxides of rare earth elements and some other

metal oxides. Since then many investigations have been reported with the rare earth metal oxides of which lanthanum and samarium oxides were studied most extensively. Perovskite type oxides have also been reported to be active for the methane coupling[21-25].

From the screening of a number of metal oxides, Keller and Bhasin[3] found that many metal oxides showed activity for the coupling reaction. Generally, metals in the most active group have multi oxidation states and most of them belong to the low melting metal part of the periodic table. PbO based catalysts have been used most often in this group since Hinsen and Baerns[11] reported their successful results with PbO.

Although the above three groups are the major groups of catalysts reported for the coupling reaction, it is often difficult to discuss each group separately because almost all types of combinations of these materials have been tried. For example, alkali-promoted rare earth metal oxides, magnesia-supported lead oxide and lanthanum oxide-supported lead oxide are all active and selective catalysts. Again, the domain of promoter and support is not clear.

Recently, more complex type of oxides have been reported for the methane coupling. Those include perovskite oxides[26], mordenite[27], layered clays[28,29] and kentrolite[30].

3. Comparison of Catalytic Performance

(a) Problems in comparison In following the studies of the methane coupling reaction comparison of the performance of a catalyst among the papers reported by different authors is frustrating. It is mainly due to the differences in the reaction conditions employed by investigators. Among the reaction conditions, W/F particularly seems to have a great effect on the C_2 yield. Otsuka and Komatsu[31] observed that the STY(space time yield) of C_2 increased from 146 to 828 $\mu mol \cdot sec^{-1} \cdot g^{-1}$ when W/F was changed from 0.012 to 0.0008 $g \cdot sec \cdot ml^{-1}$ on a Sm_2O_3 catalyst at 1023 K. Also, some papers report results with gaseous hourly space velocity(GHSV) but do not give the weight of catalyst while others report results with W/F without giving the volume of the catalyst bed. A quantitative comparison between those reports is impossible.

Other factors must also be considered in comparing the activity of catalysts. Campbell et al.[32] reported that a hydrothermal pretreatment of the

lanthanide oxides not only changed the surface areas but also changed their activities for the formation of methyl radicals. In the same paper, the authors found that Er_2O_3 obtained from one source showed only 20% of activity per unit surface area of the same oxide supplied from another source. Emesh and Amenomiya[33] reported that the preparation methods of K_2CO_3-promoted Bi_2O_3/Al_2O_3 catalyst made large differences in the yield of C_2. The initial composition of catalysts may not represent that of the working catalysts. Kimble and Kolts[34,35] observed that a 8.0wt%Li/CaO catalyst lost lithium during calcination to 4.2% and finally to 1.0% after a use for reaction. Similarly the levels of lithium in CaO catalysts with other initial Li contents were all reduced to about 1% after use. As a result, all catalysts showed similar conversion and selectivity independently of the initial concentration of Li. Roos et al.[36] also observed that a 28wt%Pb/Al_2O_3 lost Pb to 6wt% during the coupling reaction for 300 hr at 1073 K.

Because of these difficulties, reaction results obtained with a series of catalysts by the same investigators are very useful in evaluating the catalytic performance. Ito et al.[37] reported a series of MgO catalysts with various concentrations of Li. BeO catalysts promoted with various concentrations of Li were compared by Matsuura et al.[38]. Moriyama et al. [39] examined MgO promoted by alakli, alkaline earth metals and other metals at various concentrations.

The activity and selectivity of the rare earth metal oxides for the methane coupling were measured by Otsuka et al.[20,40] and compared with those of the oxides of low melting metals. Some of the rare earth metal oxides were also tested with nitrous oxide and methane[41]. Recently, Campbell et al.[32] also compared the catalytic performance of lanthanide oxides and found some differences between thier results and those of Otsuka et al.[20,40]. However, they also reported that the pretreatment of the catalysts and their source could make differences in the catalytic activity as already described. Yingli et al[42] tested some of the lanthanide oxides promoted by lithium while the effect of alkali and other metal promoters on La_2O_3 was examined by DeBoy and Hicks[43]. Otsuka et al.[44] investigated Sm_2O_3 catalyst promoted by various alkali metals.

As mentioned earlier, Keller and Bhasin[3] first screened a number of metal oxides supported on α-alumina for the oxidative coupling of methane by using a cyclic mode of reaction. In a similar redox cyclic mode, Sofranko et al.[4] tested silica-supported and unsupported metal oxides. Silica- and alumina-

supported metal oxides were also examined for the coupling reaction by Doval et al.[45]. Hinsen et al.[11] studied PbO catalysts with various support materials and different concentrations of the metal. Asami et al.[46] investigated the effect of support for PbO over a total of 23 support materials including MgO. The oxides of low melting metals of groups 13,14 and 15 in the periodic table were compared by supporting them on K_2CO_3-promoted alumina by Emesh and Amenomiya[33]. Various alkali promoters on ZnO were compared by Matsuura et al.[47] and the oxides of the first transition metals promoted by LiCl were reported by Otsuka et al.[48]. Nagamoto et al.[26] studied a series of perovskite(ABO_3) catalysts with various alkaline earth metals as A and Ti,Zr and Ce as B.

Recently Carreiro et al.[49], Burch et al.[50] and Yingli et al.[42] tested various types of catalysts under the same reaction conditions.

(b) Comparison of performance Results reported for the oxidative coupling of methane are listed in Table 1 together with the reaction conditions. All results were obtained by cofeeding the reactants and the space time yield listed is the greatest STY reported in each paper. The STY in Table 1 has been expressed as STY per gram of catalyst since this unit has been used most often in the published reports. STY/m^2 reported in some papers was converted to STY/g as long as the surface area was available. Also when possible, W/F was calculated from the flow data given. W/F is believed to be better for the comparison of the catalytic performance than the volumetric space velocity because very small amounts of catalysts were used for most of the work of methane coupling. Although the results were listed in order of STY, Table 1 should not be considered to represent the order of the catalytic performance. The reaction conditions are not the same and many other factors affect the catalytic activity as already pointed out. Large ratios of CH_4/O_2 were used in all experiments so that the conversion of oxygen was usually quite high exceeding sometimes 90%. This makes it more difficult to compare the real activity of the catalyst.

III. MECHANISM OF REACTION

1. Activation of Methane on the Surface

(a) Alkali and alkaline earth metal oxides At the high temperatures employed for the methane coupling reaction, homogeneous reactions could take place without the catalyst. Therefore, a blank test has usually been carried out before investigating catalysts to make sure that the extent of homogeneous reactions is negligible compared to the results obtained with catalysts. According to a detailed study by Yates and Zlotin[61], the homogeneous coupling of methane and formation of CO_x in an empty quartz reactor were substantial at temperatures higher than 900 K, but at lower temeratures the homogeneous reactions were much less compared to those which occured in the presence of MgO and Li/MgO catalysts. Apparently, the methane coupling reaction involves the catalyst at least at lower temperatures. The breakage of the C-H bond will be the first step in any methane activation reaction except probably for the activation by super-acid. Fang and Yeh suggested in their early report of methane coupling[19] that methyl radicals would be formed in the gas phase by the reaction of methane with the catalyst followed by their homogeneous dimerization.

The formation of methyl radicals in the gas phase was confirmed experimentally by Lunsford and his co-workers[14,65] with MgO and Li/MgO catalysts by trapping the radicals in a solid argon matrix for EPR spectroscopy. They also detected $[Li^+O^-]$ centers in lithium-doped magnesia by EPR when it was heated in air at 773 K or higher and quenched in liquid nitrogen[14,37]. The amount of methyl radicals formed and that of $[Li^+O^-]$ centers detected showed a good parallelism when the concentration of lithium was varied[14]. It was also found that the radical concentration and the conversion of methane responded similarly to the variation of oxygen pressure[37]. From these facts, Lunsford and his co-workers[37] proposed that the activation of methane takes place by abstracting hydrogen atoms on the $[Li^+O^-]$ centers. These centers are formed by oxygen vacant holes([ ]) trapped at O^{2-} ions adjacent to Li^+ ions as follows:

$$2Li^+O^{2-} + [\,] + O_2 = 2Li^+O^- + O^{2-} \qquad (1)$$

$$Li^+O^- + CH_4 \rightarrow Li^+OH^- + CH_3\cdot. \qquad (2)$$

The $[Li^+O^-]$ centers are regenerated by

$$2Li^+OH^- \rightarrow Li^+O^{2-} + Li^+[\ ] + H_2O \quad (3)$$

$$Li^+O^{2-} + Li^+[\ ] + O_2 \rightarrow 2Li^+O^- \quad (4)$$

or

$$2Li^+OH^- \rightarrow Li^+O^- + Li^+[e^-] + H_2O \quad (5)$$

$$Li^+[e^-] + O_2 \rightarrow Li^+O^-. \quad (6)$$

Thus the surface O^- species are responsible for the activation of methane. A recent work of molecular orbital theory by Mehandru et al.[66] also indicates that the abstraction of H from methane by O^- species on the surface of stoichiometric MgO has much lower activation energy than that by O^{2-} species. Driscoll et al.[14] found the O^- species by EPR on MgO as well as on Li/MgO. However, the O^- species found with MgO were very stable and did not react with methane suggesting that these species were not on the surface[14]. From the dipolar broadening of EPR signals due to the interaction between the adsorbed oxygen and the Li^+O^- centers, Wang and Lunsford[67] found that most of these centers were also in the bulk of Li/MgO.

Lunsford and his co-workers extended their studies to other alkali metal(M) promoted catalysts and found $[M^+O^-]$ centers with Li/MgO, Li/CaO[58], Na/CaO[58,60], and Li/ZnO[62]. However, they could not find $[K^+O^-]$ species on K/CaO catalyst in spite of the fact that it was active for the methane coupling[58]. No $[M^+O^-]$ centers were found on Na/MgO and K/MgO which showed poor yields of C_2 hydrocarbons[58]. These two catalysts, however, have been reported to be active for the methane coupling by Moriyama et al.[39] and Kimble and Kolts[34,35].

Other oxygen species have also been claimed to be active for the methane activation. Results obtained with BaO_2 by Sinev et al.[68] and with Na_2O_2,BaO_2 and SrO_2 by Otsuka et al.[69] indicated that the peroxide ions(O_2^{2-}) were active for the coupling reaction. The latter report also showed that the superoxide ions(O_2^-) did not activate methane. Fujimoto et al.[17] suggested that an adsorbed oxygen instead of lattice oxygen reacted with methane on alkali earth halide/alkali earth oxide catalysts. By using TPD and EPR spectroscopy Ito et

al.[70] reported that MgO could activate methane even below room temperature by dissociatively adsorbing methane heterolytically on the sites of O_{3c}^{2-}-Mg_{3c}^{2+} and O_{3c}^{2-}-Mg_{4c}^{2+}. These ion pairs are on MgO in low coordination states but their participation in the methane coupling reaction at high temperatures remains to be proved.

(b) Rare earth metal oxides Although lanthanum oxide produced a much larger amount of CH_3. radicals in the gas phase than did Li/MgO catalyst[64], the O^- species has not yet been detected by EPR on the oxides of the rare earth elements. Lin et al.[64] observed O_2^- ions when a sample of La_2O_3 was quenched from 923 K to liquid nitrogen in the presence of oxygen but not O^- species. In contrast to Li/MgO, CH_3. radicals were formed in the gas phase with La_2O_3 only when oxygen was present in the reactant stream. From these observations they suggested that the active species on this oxide were transient, namely the O^- species were formed from O_2^- during the reaction. Wang and Lunsford[71] further suggested that the superoxide ions are in equilibrium with the surface peroxide ions and oxygen,

$$O_2 + O_2^{2-} = 2O_2^-.$$

Otsuka and Nakajima[72] also could not detect the O^- ions in samarium oxide by EPR. Without detection of the species, Otsuka et al.[40] assumed that [$Sm^{3+}O^-$] species were active centers on Sm_2O_3. In another work on Sm_2O_3[73], Otsuka and Jinno concluded from the observed kinetics of the methane coupling that an adsorbed diatomic oxygen instead of monoatomic oxygen was the active species. This seems to agree with Lunsford et al.[64], i.e., the transient O^- species are formed from O_2^-. In any case, an important difference between the rare earth metal oxide and alkali/alkaline earth oxide catalysts is that the active oxygen species on the rare earth oxides are a sorbed form of oxygen while those in the latter catalysts are a part of the lattice as pointed out by Lunsford and his co-workers[64].

(c) Other oxides The process of activation of methane and the oxygen species responsible for the activation on other metal oxides are not clear. Driscoll and Lunsford[65] found with the technique of radical trapping in solid argon matrix

that Bi_2O_3, α-Bi_2O_3-MoO_3 and PbO produced none or much less $CH_3\cdot$ radicals in a stream of methane at 748 K compared to MgO and Li/MgO. However, these oxides were active for the formation of allyl radicals from propylene and they suggested that hydrogen atom was abstracted by lattice O^{2-} ions in sites of low coordination. Sinev et al.[52] also suggested that O^{2-} ions with reduced coordination would be responsible for the methane coupling reaction on PbO/Al_2O_3 catalyst. Suleimanov et al.[74] studied PbO/MgO catalysts by EPR and found that a paramagnetic center due to $[PbO_4]^-$ increased noticeably upon heating at 1023 K and that these centers disappeared when the catalyst was contacted with methane at 1023-1073 K. They further observed that the methane conversion was parallel to the concentration of the centers.

By using a lead mirror, Jones et al.[5] observed the formation of free radicals in the gas phase, most likely methyl radicals, on a sodium-promoted manganese/silica catalyst.

2. Reaction Mechanism

When Ito and Lunsford[15] first reported that lithium-doped magnesia was an efficient catalyst for the methane coupling, they assumed the formation of CH_3 radicals on the surface $[Li^+O^-]$ centers and subsequent coupling of the radicals in the gas phase. Indeed, Campbell et al.[75] later measured the concentration of CH_3 radicals trapped directly from the atmospheric coupling reaction on Li/MgO and demonstrated that the rate of decay of the radicals was of second order for their concentration as shown in Fig.2.

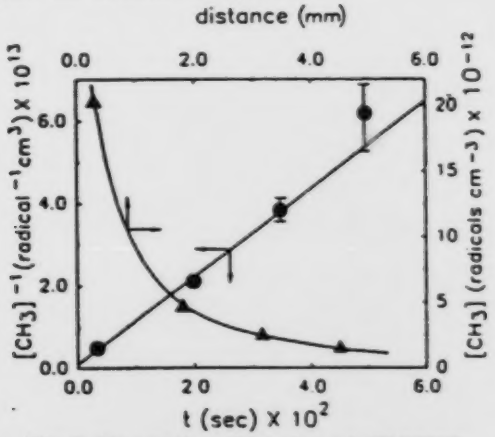


Fig.2 Second order plot of CH3[75]

Here, we will follow the mechanism of the methane coupling proposed for Li/MgO and Na/CaO catalysts by Lunsford and his co-workers[37,60]. Following eqs.(1)-(6) already described,

$$2CH_3\cdot \rightarrow C_2H_6. \qquad (7)$$

The methyl radicals also produce CO_x through a series of chain reactions in the gas phase,

$$CH_3\cdot + O_2 = CH_3O_2\cdot \qquad (8)$$

$$CH_3O_2\cdot + C_2H_6 \rightarrow CH_3O_2H + C_2H_5\cdot \qquad (9)$$

$$2CH_3O_2\cdot \rightarrow CH_2O + CH_3OH + O_2 \rightarrow CO, CO_2 \qquad (10)$$

$$CH_3O_2H \rightarrow CH_3O\cdot + OH\cdot \qquad (11)$$

$$CH_3O\cdot + CH_4 \rightarrow CH_3OH + CH_3\cdot \qquad (12)$$

$$OH\cdot + CH_4 \rightarrow CH_3\cdot + H_2O \qquad (13)$$

or on the surface

$$CH_3\cdot + O^{2-}(surface) \rightarrow CH_3O^{-}\cdot + e^{-} \qquad (14)$$

$$CH_3O^{-}\cdot \rightarrow CH_3OH, CH_2O \rightarrow CO, CO_2. \qquad (15)$$

Ethane produced by the coupling reaction further reacts to form ethylene either on the surface,

$$C_2H_6 + [M^{+}O^{-}] \rightarrow C_2H_5\cdot + [M^{+}OH^{-}]_s \qquad (16)$$

$$C_2H_5\cdot + O^{2-} \rightarrow C_2H_5O^{-} + e^{-} \qquad (17)$$

$$C_2H_5O^- \rightarrow C_2H_4 + OH^- \quad (18)$$

or in the gas phase through eqs.(9), (19), (20) and (21),

$$CH_3\cdot + C_2H_6 \rightarrow CH_4 + C_2H_5\cdot \quad (19)$$

$$C_2H_5\cdot \rightarrow C_2H_4 + H\cdot \quad (20)$$

$$C_2H_5\cdot + O_2 \rightarrow C_2H_4 + HO_2\cdot. \quad (21)$$

The above mechanism has been summarized by Lin et al.[60] in a scheme shown in Fig.3.

The major features of the above mechanism are:(1) methyl radicals are formed catalytically and dimerize in the gas phase producing ethane;(2) the formations of ethane and of CO_x are parallel reactions;(3) ethylene is formed from ethane as a secondary product; and (4) the reactions involved in (2) and (3) also take place heterogeneously and/or homogeneously. Sofranko et al.[4] observed that the hydrocarbon distribution was remarkably similar in the products with various supported metal catalysts and with an empty reactor. From this fact they considered that the gas reactions are responsible for carbon building after the methane activation on the surface. Most of the results of the methane coupling obtained on various catalysts have been explained by a similar mechanism although

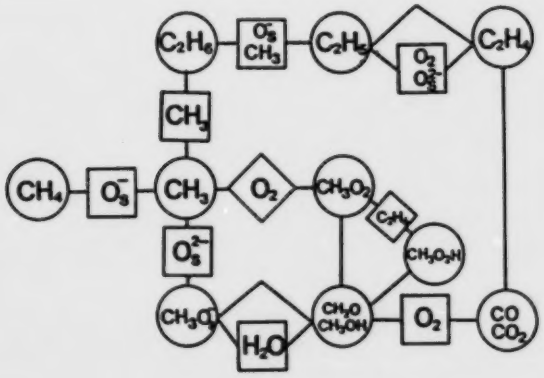


Fig.3 Reaction scheme[60]

the details of the mechanisms are not always the same. Catalysts for which the reaction mechanism was discussed were La_2O_3 by Lin et al.[64], Sr/La_2O_3 by Deboy and Hicks[76], Sm_2O_3 by Otsuka et al.[40,72,73], Li/ZnO by Zhang et al.[62], $Na/Mn/SiO_2$ by Jones et al.[8], Mn/SiO_2 by Sofranko et al.[4], Sb_2O_3 by Lo et al.[13] and Pb/Al_2O_3 by Sinev et al.[52].

Other mechanisms have also been proposed for the formation of ethane and other parts of the reaction. Lunsford and his co-workers[64] suggested the possible involvement of carbene(CH_2) for the formation of ethylene, although carbene was not detected by argon matrix isolation. From the facts that the concentration of $CH_3\cdot$ radicals in the gas phase is very low and that the O^- species are not found on some catalysts active for the methane coupling, Martin and Mirodatos[77,78] proposed the carbene as the intermediate for the formation of ethane on Li/MgO,

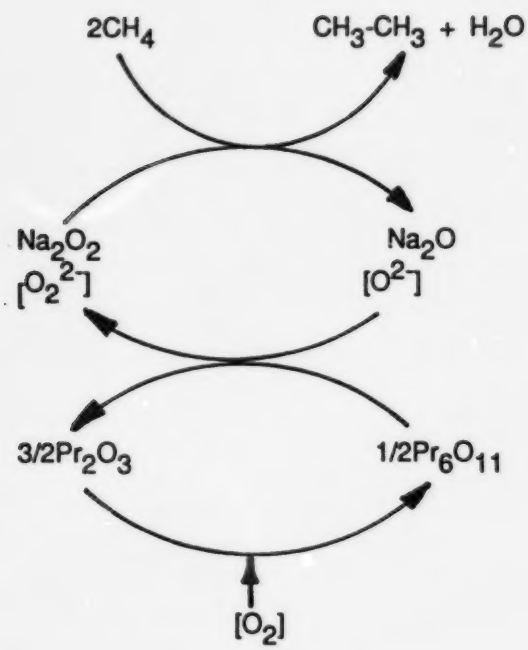
$$CH_4 + O^{2-} \rightarrow CH_3^- + OH^- \qquad (22)$$

$$Li^+ + CH_3^- \rightarrow Li^+H^- + CH_2\cdot \qquad (23)$$

$$CH_2\cdot + CH_4 \rightarrow C_2H_6\cdot \qquad (24)$$

They estimated the amount of carbene in the gas phase from cyclopropane formed on the addition of ethylene.

A catalytic formation of ethane by a dissociative adsorption of methane was proposed on K-promoted Bi_2O_3/Al_2O_3 by Emesh and Amenomiya[33] and on Li/BeO by Doi et al.[79]. Asami et al.[80] also claimed that the dimerization of methyl radicals on PbO/MgO catalyst mostly took place on the surface. Based on the reactivity of the peroxide anion(O_2^{2-}) reported by Otsuka et al.[69], Gaffney et al.[6] recently proposed a mechanism for the methane coupling on Na/Pr_2O_3 as depicted below.



In the above mechanism, Na_2O is oxidized back to Na_2O_2 by oxygen supplied from praseodymium oxide which in turn is reoxidized by O_2 in the gas phase.

Hutchings et al.[81] concluded that ethylene and ethane were both primary products on Li/MgO. From the comparison of oxidants, they also concluded that the $O\cdot$ species lead to CO_x while the O^-species was responsible for the C_2[81]. At high temperatures, however, the O^- was thought by the same authors[82] to contribute to the formation of CO_x. With the aid of TPD, Tagawa and Imai[22] revealed two kinds of oxygen adsorbed on $LaAlO_3$, and found that the C_2 hydrocarbons were formed by the strongly adsorbed oxygen while the weakly adsorbed or gaseous oxygen was responsible for CO_x. Gaffney et al.[6] thought that CO_x was formed on Na/Pr_2O_3 predominantly on the surface via allylic oxidation of olefins. Asami et al.[80,83] concluded that on PbO/MgO CO_x was due to a reaction between methane and oxygen adsorbed on PbO.

Temperatures used for the oxidative coupling of methane are quite high so that many authors observed or assumed that the water-gas shift reaction is in equilibrium among CO, CO_2, H_2 and H_2O[62,76,84,85]. Imai et al.[12] also thought that the steam reforming reaction of methane took place on $LaAlO_3$ at these temperatures.

(3) Rate-Determining Step

When Lunsford and his co-workers proposed the mechanism(reactions(1)-(21)), they assumed that the rate-determining step was the regeneration of the [Li^+O^-] centers(reactions(3)-(6)) which required high temperature. Amorebieta and Colussi[86] claimed that the C-H bond breaking, namely the abstraction of H atom, was the rate-determining step on Li/MgO. The pressure they used, however, was extremely low(less than 0.1 torr) so that the conclusion may not be applied to other cases. From the observed isotope effect between CH_4 and CD_4 in the methane coupling on MgO and Li/MgO catalysts, Buevskaya et al.[87] and Cant et al.[88] both concluded the H-abstraction(reaction(2)) to be the rate-determining step. Reaction(3) will also exhibit an isotope effect, but the latter authors found no isotope effect by feeding CH_4+D_2O. Otsuka et al.[73] also concluded from the observed kinetics that the abstraction of hydrogen atom was the slowest step on Sm_2O_3. When the methane coupling reaction was carried out with N_2O on the same catalyst, the rate-determining step shifted to the decomposition of N_2O[72].

In a study of the gas phase coupling reaction of methane, Lane and Wolf[89] found the apparent activation energy of methane conversion to be 228kJ/mol and pointed out that it was similar to the activation energies(234-240kJ/mol) reported for the formation of methyl radical in the gas phase from methane and molecular oxygen:

$$CH_4 + O_2 \rightarrow CH_3\cdot + HO_2\cdot. \qquad (25)$$

As they discussed, the value they observed was also close to the activation energy observed with various catalysts for the methane conversion[37,91] and for the C_2 formation[13,79,83]. If reaction(25) is the rate-determining step of the catalytic coupling reaction, however, the role of the surface O^- becomes uncertain.

Mirodatos and Martin[78] observed in a transient experiment on Li/MgO that the formation of C_2 continued after the supply of oxygen was cut while the C_2 formation stopped immediately after cutting the methane supply. From these observations, they concluded that the oxygen supply was not the rate-determining step. Lin et al.[60], however, concluded that it depends on the pressure of

oxygen and that the rate-determining step could be the oxygen supply when the oxygen pressure was lower than 20 torr.

(4) Kinetics

It is not easy to obtain kinetic equations experimentally for the methane coupling reaction mainly because of the high conversion of oxygen. While Otsuka et al.[73] experimentally determined the rate of total methane conversion on a samarium oxide catalyst as a function of the pressures of the reactants, several other authors established kinetic models based on the mechanism similar to that described in Section(2) of this Chapter. The methane conversion and the C_2 selectivity were then derived from these equations mostly by taking the rate constants of homogeneous reactions from published values and by usually determining the rate constants of heterogeneous reactions to best fit the experimental data. The derivation of these kinetic expressions was reported for Li/MgO by Kimble and Kolts[34], for Mn/MgO by Labinger and Ott[90], for Li/MgO by Amorebieta and Colussi[86], for PbO/MgO by Asami et al.[83] and for various catalysts by Sinev et al.[91.92].

The reaction orders have also been determined by many investigators for the simple expression by power law, namely rate=$k(P_A)^a(P_B)^b$. The observed data are collected in Table 2 where the reaction orders for the formations of C_2 and CO_x and also those for the dehydrogenation of ethane are listed. Also included in Table 2 are the apparent activation energies(kJ/mol) for the reactions where available. However, the reaction orders for the total methane conversion were not included.

IV OPTIMIZATION OF REACTION CONDITIONS

(1) Characterization of Catalysts

The effect of the concentration of metal oxides on supports and of the concentration of pomoters have been investigated by many workers as already described in II.(3)a. Characterization of catalysts leading to the identification

of active sites is essential to prepare efficient catalysts for the methane coupling. As described in the previous chapter, Lunsford and his co-workers used EPR spectroscopy extensively to identify the active centers. Among the various techniques used for the characterization of catalysts, XRD has been employed most often. Thus Matsuura et al.[38] identified $Li_2Be_2O_3$ as the active species on Li/BeO catalyst. Iwamatsu et al.[93] found that the lattice distortion as measured by the line-broadening of XRD and the surface area was related to the activity of alkali-doped MgO catalysts. From the intensity of a photoluminescence band appearing on Li/MgO catalysts at 450 nm, Anpo et al.[94] concluded that the low coordinate surface sites formed by the addition of Li played an important role in the coupling reaction. The state of lithium compound on MgO was studied by Kimble and Kolts[35].

Investigating a series of lanthanide oxides for the methane coupling, Campbell et al.[32] found that the activity increased with increasing basicity of the oxides except for those metals with multiple stable oxidation states. In a study of a series of perovskite(ABO_3) catalysts, Nagamoto et al.[26] concluded that the basicity of A ion in the oxide is closely related to the catalyst activity per unit surface area. Imai et al.[23] found with LaAlO3 catalyst that the amorphous phase of the oxide was active, and that the C_2 yield dropped as the crystalization to perovskite grew. For Ce_2O-Yb_2O_3(fluolite) and SrO-CeO_2(perovskite) catalysts, Machida and Enyo[25] observed that the ion conductivity either by O^{2-} or by H^+ showed a maximum or minimum, respectively, in the selectivity vs composition curves. Ce^{4+} was identified as the active species on Ba/CeO_2 catalyst by Otsuka et al.[51] while the surface Mg_6MnO_8 species was found to be active for the methane coupling in Mn/Mg mixed oxide by Labinger et al.[95]. Lo et al.[13] identified α-Sb_2O_4 to be the only antimony phase in K-doped antimony catalysts which gave a high selectivity under the reaction conditions.

At the high temperatures employed for the methane coupling reaction, the stability of the catalyst is an important factor for the practical catalysts. Lithium is a widely used promoter, but it is lost at high temperatures because of its volatility[34,35,55]. Korf et al.[96] observed that the yield of C_2 on Li/MgO at 1073 K increased a little for the first 2 hr and then dropped continuously levelling off finally after 40 hr. In a test of the life of Na/Pr_6O_{11}, Gaffney et al.[6] found that the methane conversion remained almost constant over a period

of 3200 hr while the C_2 selectivity dropped from 63 to 54% between 50 and 100 hr. On the other hand, Lin et al.[60] observed a decrease in the formation of CO_2 on Na/CaO catalyst for the first 10 hr while the C_2 formation unchanged up to 40 hr. As a result, the C_2 selectivity increased initially. No significant loss of Na was observed.

(2) Selectivity

The C_2 selectivity is undoubtedly the most important aspect of the oxidative coupling reaction of methane. When the reactants are recycled through the catalyst bed to increase the yield of C_2, the selectivity must be high if the conversion is not the highest. Many authors have discussed the selectivity in terms of the surface properties of the catalyst, the reaction conditions and of the mechanism. As one of the features of the methane coupling, it is often observed that the selectivity increases with increasing temperature[15,33,37,40,46,52,60,64,73]. It is expected because the activation energy of C_2 formation is usually much higher than that of CO_x formation as seen in Table 2. Therefore, more C_2 is produced at high temperature than CO_x. Lin et al.[60] also pointed out that the formation of C_2 is of second order for $CH_3\cdot$ radicals(reaction(7)) while that of CO_x is of the first order(reactions(8) and (14)). When more $CH_3\cdot$ radicals are produced at higher temperature, therefore, the increase in C_2 becomes more than that in CO_x.

Higher selectivity at lower oxygen pressure was also observed by Lin et al.[64] and by Otsuka et al.[73] on lanthanide oxides catalysts. As seen again in Table 2, the reaction order of oxygen for the C_2 formation is generally lower that that for the CO_x formation so that CO_x becomes predominant at higher oxygen pressure. Sinev et al.[91,92] derived the limiting selectivity as a function of oxygen pressure which also indicated the decrease in selectivity with higher pressure of oxygen. Since the secondary oxidation of C_2 products to CO_x is fast, higher selectivities are expected at lower conversions with the lower pressures of oxygen[64,73]. In the coupling reaction with a mixture of CH_4+O_2, the gaseous oxygen is responsible not only for the regeneration of the active oxygen species on the surface but also for the formation of CO_x. Aika and Nishiyama[63,97] discussed the use of CO_2 as an oxidant which oxidizes only the surface sites.

Hinsen et al.[11] claimed that the non-selective oxidation of methane took

place on the acid sites of the catalyst. Other authors also concluded that the CO_x formation was related to the acidity of catalysts[5,46,48,49,50,56]. For alkali-promoted lanthanide oxides, one of the functions of alkali promoter was considered to be the poisoning of the sites for the non-selective oxidation thus improving the selectivity[50,51]. Zhang et al.[62] observed with Li/ZnO that the support ZnO acted as a sink of methyl radicals and that Li poisons that function. Sinev et al.[52] concluded that on PbO/Al_2O_3 catalyst PbO destroy methyl peroxide radicals($CH_3O_2\cdot$) which lead to the formation of CO_x. Some investigators found, however, that the reduction of acidity does not reduce the CO_x production nor improve the selectivity[13,33,62].

The suface area of the catalyst also seems to be an important factor for the selectivity and the yield of the coupling reaction. Iwamatsu et al.[84,93] found with Na/MgO catalysts that the catalysts with smaller specific surface area generally gave higher yield of C_2. Lin et al.[60] observed on Na/CaO catalysts that the addition of Na reduced the surface area of the catalysts minimizing the non-selective oxidation and increasing the selectivity. The reduction of the surface area by adding a proper amount of sodium to Mn/SiO_2 catalysts was one of the major factors for a high yield of C_2 as observed by Jones et al.[5].

Ethylene is, of course, a more valuable product than ethane in the oxidative coupling of methane. Otsuka et al. reported a high ratio of ethylene/ethane on $LiCl/Sm_2O3$[57] and LiCl-promoted first transition metal oxides[48] while Fujimoto et al.[17] also observed high selectivity to ethylene on alkali halides-promoted CaO and MgO catalysts. It is interesting to see that both groups used alkali halides as promoters. Kimble and Kolts[34] found on alkali metal-promoted alkaline earth metal oxides that ethylene increased at the sacrifice of ethane when the ratio of steam/CH_4 was increased.

(3) Other Operating Factors

All reactions listed in Table 1 were carried out with oxygen as an oxidant. Nitrous oxide has also been used as an oxidant for the methane coupling. Kowalak and Moffat[27] studied the reaction of CH_4+N_2O on mordenite catalysts and Meng and Sanger[98] examined the coupling reaction on supported PbO and SnO catalysts with nitrous oxide. Results of Otsuka and Nakajima[41] obtained on the rare earth metal oxides showed that the reactivity of N_2O was much lower than that of O_2 but

that the selectivity was higher with N_2O particularly at low temperatures. Hutchings et al.[81,99] also observed on unpromoted and Li-promoted MgO that nitrous oxide was less reactive than oxygen. However, the effect of the oxidant on the selectivity seems to depend on temperature and on the presence of the promoter.

As already described, the homogeneous reactions are involved in the oxidative coupling of methane, and their contributions to the overall reaction become greater at high temperatures [4,61,89]. The temperature range in which the gas phase reactions become predominant seems to shift to lower temperatures at elevated pressures. In their investigation up to 585 kPa, Hutchings et al.[100] found that the gas phase reactions dominated even at 810 K when the pressure was 335 kPa or higher. As a result, there was only minor differences between the presence and the absence of a Li/MgO catalyst. Asami et al.[101] studied the homogeneous coupling reaction under still higher pressures and observed that the ratio of ethylene/ethane increased with the pressure but that the C_2 selectivity decreased from 60% at 0.35 MPa to 45% at 1.6 MPa with a marked increase in the formation of CO.

The effect of reaction conditions and of the reactor's materials on the homogeneous coupling reaction was studied by Lane and Wolf[89]. Because of the presence of the gas phase reactions, the empty space in the reactor affects the reaction. van Kasteren et al.[102] investigated the effect of the space behind the catalyst bed and recognized that the homogeneous dehydrogenation of ethane took place in the space when no oxygen remained. In the presence of oxygen, however, they found that the empty space behind the catalyst acted as an afterburner of hydrocarbons.

Some attempts have been made to control the oxygen supply electrochemically for better selectivity of the coupling reaction[103,104,59]. All used a solid electrolyte(zirconia) on which a catalytic material such as Ag/Bi_2O_3 and $LiNiO_2$ were deposited.

V. METHANE CONVERSION VIA OXYCHLORINATION

Oxychlorination(oxyhydrochlorination) is an oxidative condensation of a molecule with chlorine(hydrogen chloride) by adding oxygen. One of the industrial

applications of this process is the production of vinyl chloride monomer from ethylene, hydrogen chloride and oxygen. When olefin is replaced by methane, chloromethanes are formed under moderate conditions. Catalysts, mainly $CuCl_2/KCl/SiO_2$, have been developed for this process recently[105,106]. It is also known that methyl chloride is oligomerized by dehydrohalogeno-condensation to higher hydrocarbons over oxide catalysts such as silica-alumina[107]. The yield of higher hydrocarbons over silica-alumina, however, is not very high because of a high conversion to methane. Methyl chloride is a monofunctionalized methane, therefore, its oligomerization can be carried out efficiently by the ZSM-5 catalyst similar to the case of methanol[108]. A methane conversion process recently proposed by the Pittsburgh Energy Technology Center[109] combines the above two processes, the oxychlorination with $CuCl_2/KCl/SiO_2$ and the oligomerization with ZSM-5, in series. The temperature is modest(600 K) and the products are mainly aromatics.

As described in the Introduction section, the oxidative coupling of methane is also thermodynamically feasible with Cl_2 instead of O_2. A patent claimed a non-catalytic process in which a mixture of natural gas and chlorine was reacted at high temperatures(970-1980 K) to produce higher hydrocarbons, mainly ethylene and hydrogen chloride[110]. Hydrogen chloride is oxidized back to chlorine(Deacon reaction) so that the overall reaction becomes identical with the coupling reaction with oxygen. Shigapov et al.[111] suggested for the oxidative coupling of methane carried out on a $CaCl_2/CaO$ catalyst that chlorine generated by the catalyst surface participated in the formation of C_2 in the gas phase.

VI. CONCLUSIONS AND RECOMMENDATIONS

The oxidative coupling of methane is one of the promising processes for converting methane into higher hydrocarbons. As reviewed above, the process has some shortcomings as well as good features. The reaction is relatively easy to carry out without too many problems of corrosion to the reactor materials, and high C_2 yield(>20%) and very high selectivity(>90%) have been achieved. On the other hand, the reaction requires high temperatures and the products are almost limited to C_2. The mechanism of the reaction is rather complex in the sense that

it proceeds both heterogeneously and homogeneously. That the blank test without catalyst produces very little or negligible amount of reaction products is somewhat misleading. The reaction in the empty reactor is limited by the poor production of $CH_3\cdot$ radicals. Once the formation of the radicals is initiated by a catalyst, the gas phase reactions proceed extensively.

It can be seen in Table 1 that most of the large space time yields have been obtained with very small W/Fs and that this trend is observed over the entire range of W/F. The STY is also affected by the partial pressures of the reactants. In order to eliminate these effects the STY was divided by the partial pressure of methane and listed in Table 3 as activity because the C_2 formation is close to the first order for the methane pressure as seen in Table 2. The effect of oxygen was not corrected since the reaction order of oxygen is usually small(Table 2). The activity listed in Table 3 has been expressed in a different unit from that used in Table 1, ml instead of μmol. The activity thus derived may be regarded as the rate constant of the catalyst if the overall reaction is treated as a first order catalytic reaction. Again higher activities are observed with smaller W/Fs. The activity is plotted against W/F in Fig.4 which shows a good linear relationship over four orders of magnitude of variation in W/F. Also the linearity is held independent of the catalyst used as seen in the figure. If the reaction is controlled by a catalytic process, the activity should be constant indepedent of W/F, but should depend on the catalyst. Fig.4 seems to indicate that the yield of C_2 is governed mostly by the gas phase reactions instead of catalytic ones. A study by Mtsuura et al.[38] on Li/BeO catalysts clearly indicated that the reaction rate was approximately proportional to the amount of catalyst at low temperatures but that, at high temperatures, the rate became independendent of the catalyst amount.

From the above point of view, a great effort in developing new catalysts or in improving catalysts may not be rewarding as far as the C_2 yield is concerned. Instead, investigations in the engineering aspects of the process will be more fruitful. We recommend researches which clarify quantitatively the extent of contributions made by the gas phase and the surface. Such researches should include experiments in which the amount of catalyst is varied in a constant volume of the catalyst bed or the volume of the catalyst bed is varied with a constant amount of catalyst. Very few work has been done on this matter so far.

The conversion of methane through oxychlorination is interesting enough to

watch the future development. This route consists, at this moment, of two processes and is not a direct conversion. There might be a corrosion problem as well. Nevertheless, the route is attractive because the main product is the gasoline-range liquid instead of C_2. However, the investigations of these processes have begun recently, and it is too early to assess the feasibility.

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Table 1. COMPARISON OF CATALYTIC PERFORMANCE

'CATALYST	Temp. (K)	P(CH4) (atm)	P(02) (atm)	W/F (g.sec/ml)	Sel. (%)	Yield (%)	STY (μmol/sec/g)	Ref.#
Sm2O3	1023	0.859	0.143	0.0008	63	3.5	828	31
20(mol%)Ba-CeO2	1023	0.72	0.276	0.0022			263.9	51
3(mol)%Li-BeO	1033	0.75	0.247	0.012	63.1	15.3	215.6	38
3mol%Li-BeO	1033	0.75	0.25	0.012	63.1	15.2	214.2	79
1(wt%)Sr-La2O3	1023	0.3	0.05		74.4	9.23	129.2	43
20(wt)%PbO-Al2O3	973	0.575	0.09	0.0118	47.4	5.3	57.82	52
LaAlO3(mist deposit)	983	0.7	0.07	0.0234	39.2	7.2	48.21	24
Nd2O3	973	0.373	0.03	0.006	62.5	2.75	38.13	32
9(wt)%K2CO3-7(wt)%Bi2O3-Al2O3	913	0.5	0.05	0.0105	29	2.1	22.5	33
20(mol)%NaCl-manganese oxide	1023	0.667	0.333	0.15	43.4	13.9	17.778	53
3.5%Na2CO3/CaO	1023	0.691	0.074	0.14	78	11.7	12.89	49
10wt%Mn-5wt%Na4P2O7-SiO2	1073	0.5	0.1	0.074	48	5	7.577	54
5.3(wt)%Li-MgO	1076	0.5	0.105	0.219	54	12.4	6.318	36
20(wt)%BaO-CaO	1073	0.395	0.066	0.215	61.1	14.2	5.81	16
16%Li2O/TiO2(16% as Li)	1073	0.32	0.08	0.15	75	11.3	5.36	55
36(wt)%PbO-Al2O3	1013	0.691	0.069	0.22	56.2	5	3.507	56
3(wt)%Na-Pr6O11	1173	0.5	0.1	0.921	63.9	13.9	1.689	6
SrCe0.90Yb0.1O2.95	1023	0.133	0.067	0.72	60.1	31.6	1.306	25
20(wt)%PbO-MgO	1023	0.138	0.016	0.161	65.5	6.6	1.26	46
5(wt)%MgCl2-CaO	1023	0.128	0.014	0.161	87.1	7	1.24	17
SrZrO3	1023	0.158	0.079	0.4		11.7	0.92	26
5(atom)%K-Sb2O4	1053	0.5	0.111	0.333	52	2.5	0.837	13
20(mol)%LiCl-MnO2	1023	0.05	0.025	0.6	64.7	30.6	0.57	48
LaAlO3(mist deposited)	1033	0.5	0.1		32.3		0.42	23
20(mol)%LiCO3-Sm2O3	1023	0.05	0.02	0.6	54.1	22.3	0.415	57
Ca/Layered bisauth oxychloride	996	0.197	0.099	2.4	68.7	19.9	0.36	28

7(wt)%Li-MgO	973	0.1	0.049	0.87	56.7	12.8	0.328	58
LiNiO2	973	0.232	0.038	0.171	48		0.32	59
12.5(mol)%Li-ZnO	1013	0.108	0.057	2.4	66.8	23.9	0.239	47
15(wt)%Na-CaO	998	0.15	0.147	2.17	38.3	14.8	0.228	60
3%Li-MgO	973	0.28	0.136	4.92	37.6	14.8	0.188	61
Sm2O3	1023	0.18	0.035	2.4	60.6	9.2	0.153	40
0.18(wt)%Li-ZnO	1023	0.1	0.05	4.8	53.3	15	0.07	62
7(wt)%Li-MgO	993	0.076	0.047	4.819	45.4	19.4	0.069	15
15(mol)%Na-MgO	1073	0.027	0.014	2.172	56.8	22.4	0.063	39
2(mol)%K-BaCO3	1073	0.027	0.014	2.172	42	20.2	0.056	18
50%PbO-MgO	1073	0.083	0.001	2		4.37	0.041	63
La2O3	998	0.075	0.022	2.381	23.7	4.67	0.033	64

Table 2. REACTION ORDERS

Rate=$kP_A^aP_B^b$; m:methane o:oxygen e:ethane; ( ):activation energy]kJ/mol]

Catalyst	Temp (K)	$CH_4 \rightarrow C_2$		$CH_4 \rightarrow CO_x$		$C_2H_6 \rightarrow C_2H_4$		Ref.
		m	o	m	o	e	o	
Li/MgO	900-1050	0.75 (169)	0.1~-0.2	-0.1 (90-118)	0.8	0.4 (140-250)	-0.05	78
Li/BeO	953	1.0 (246)	0.3~0.5	0 (103)	1.0	0.5 (127)	0.5	79
$LaAlO_3$	983	0.9~1.0	0.5~1.2	0.1~0.7	1.4~1.7	$CH_4/O_2 > 4$		22
〃		1.7~1.9	-0.8~0.7	0.7~0.9	0.5~1.2	$CH_4/O_2 < 4$		〃
PbO/Al_2O_3	1013	0.8 (99)	1.1	0.4 (51)	1.5	0.8 (6)	1.6	11
PbO/Al_2O_3	953-1073	1.07	1.4	0.6~1.0	2.0~0.34			49
K/Sb_2O_4	1023-1073	0.6 (259)	0.2	0.1 (96)	0.8			13
Sb_2O_4	1023-1073	0.9 (234)	0.5	0.4 (95)	0.8			〃
$K/Bi_2O_3/Al_2O_3$	823	2	1	0.3	1	1	2.5	33
PbO/MgO	1023	0.9 (210)	0	0.4 (108)	0.7	1	0	83

Table 3. COMPARISON OF ACTIVITY OF CATALYST

CATALYST	W/F	TEMP[K]	ACTIVITY	Ref.
Sm_2O_3	0.0008	1023	43.19	31
1(wt%)Sr-La_2O_3		1023	19.29	43
20(mol%)Ba-CeO_2	0.0022	1023	16.4	51
3(mol)%Li-BeO	0.012	1033	12.88	38
3mol%Li-BeO	0.012	1033	12.85	79
Nd_2O_3	0.006	973	4.583	32
20(wt)%PbO-Al_2O_3	0.0118	973	4.507	52
$LaAlO_3$(mist deposit)	0.0234	983	3.086	24
9(wt)%K_2CO_3-7(wt)%Bi_2O_3-Al_2O_3	0.0105	913	2.016	33
20(mol)%NaCl-manganese oxide	0.15	1023	1.194	53
3.5%Na_2CO_3/CaO	0.14	1023	0.836	49
16%Li_2O/TiO_2(16% as Li)	0.15	1073	0.75	55
10wt%Mn-5wt%$Na_4P_2O_7$-SiO_2	0.074	1073	0.679	54
20(wt)%BaO-CaO	0.215	1073	0.66	16
5.3(wt)%Li-MgO	0.219	1076	0.564	36
20(mol)%LiCl-MnO_2	0.6	1023	0.51	48
$SrCe_{0.90}Yb_{0.10}O_{2.95}$	0.72	1023	0.439	25
5(wt)%$MgCl_2$-CaO	0.161	1023	0.434	17
20(wt)%PbO-MgO	0.161	1023	0.41	46
20(mol)%$LiCO_3$-Sm_2O_3	0.6	1023	0.372	57
$SrZrO_3$	0.4	1023	0.261	26
36(wt)%PbO-Al_2O_3	0.22	1013	0.227	56
3(wt)%Na-Pr_6O_{11}	0.921	1173	0.151	6
7(wt)%Li-MgO	0.87	973	0.147	58
15(mol)%Na-MgO	2.172	1073	0.103	39

12.5(mol)%Li-ZnO	2.4	1013	0.1	47
2(mol)%K-BaCO3	2.172	1073	0.093	18
Ca/Layered bismuth oxychlorid	2.4	996	0.083	28
5(atom)%K-Sb2O4	0.333	1053	0.075	13
15(wt)%Na-CaO	2.17	998	0.068	60
7(wt)%Li-MgO	4.819	993	0.04	15
Sm2O3	2.4	1023	0.038	40
LaAlO3(mist deposited)		1033	0.037	23
0.18(wt)%Li-ZnO	4.8	1023	0.031	62
3%Li-MgO	4.92	973	0.03	61
50%PbO-MgO	2	1073	0.022	63
La2O3	2.381	998	0.0196	64

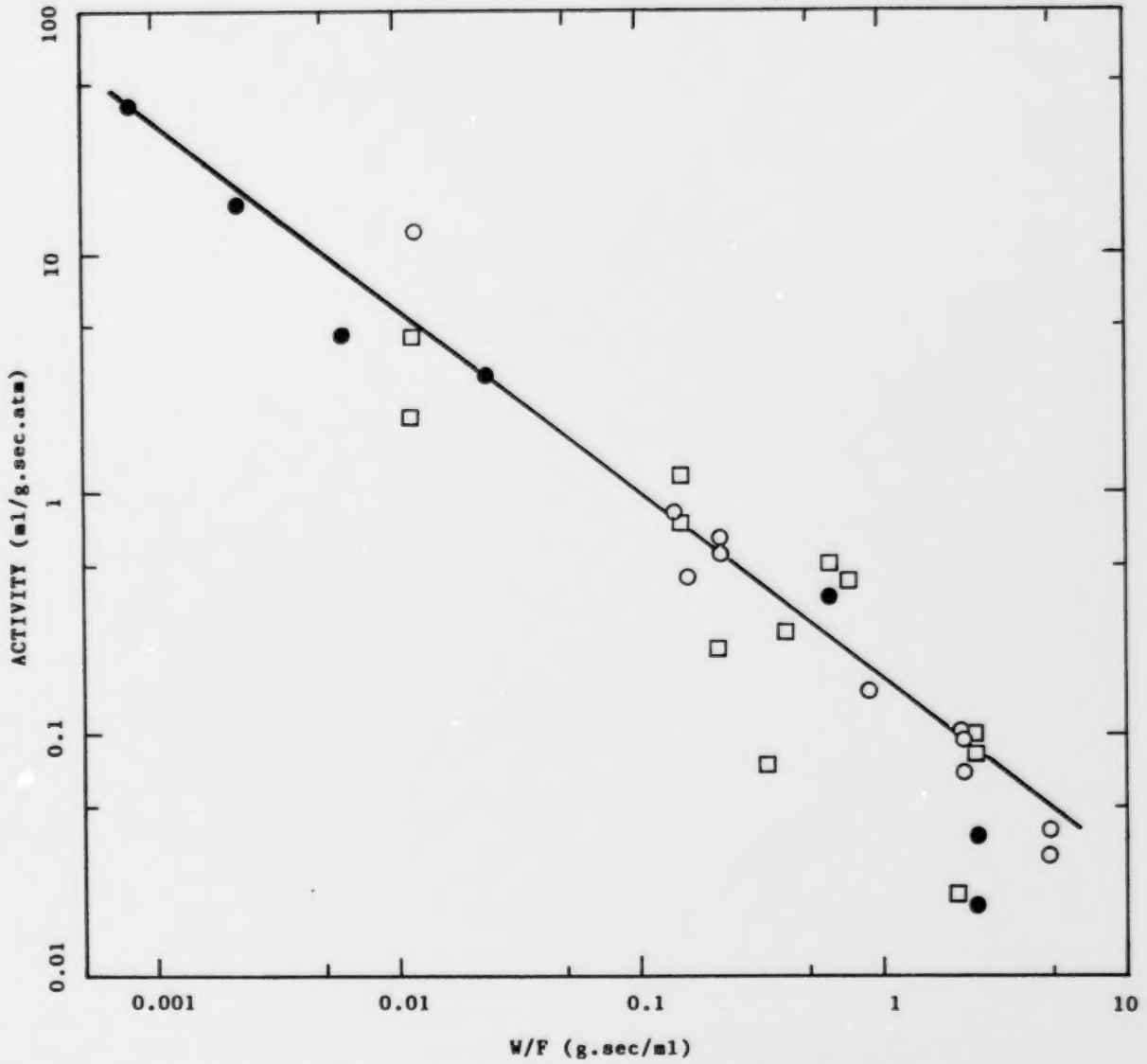

Fig.4 Activity vs W/F. ○ Alkali/alkali earth metals; ● rare earth metals; □ other oxides